Flammability and Consequence Analysis for MCU Waste Tanks

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Abstract

The Savannah River Site of Department of Energy will use the new Modular Caustic Side Solvent Extraction Unit (MCU) to process the waste stream by removing/reducing Cs-137 using Caustic Side Solvent Extraction (CSSX) technology. The CSSX technology utilizes multi-component organic solvent and annular centrifugal contactors to extract Cs-137 from waste salt solution. Due to the radiolysis of the aqueous nuclear wastes, hydrogen generation is expected in the MCU holding tanks. The hydrogen from radiolysis and the vapor from the organic component of the solvent, Isopar-L, may form a composite flammable gas mixture, resulting in a shorter time to flammability than that of a pure hydrogen environment. It has been found that the time-to-Lower Flammability Limit (LFL) and stoichiometric concentration (SC) vary greatly from tank to tank, and could be decreased significantly by the presence of the Isopar-L. However, neither the deflagration nor the detonation event would challenge the Evaluation Guideline for any of the tanks at any liquid level.

Introduction

The MCU is part of the process used for disposal of liquid waste at the Department of Energy Savannah River Site (SRS). The MCU will process the waste stream by removing Cs-137 from the salt solution in preparation for final disposal in grouted vaults using CSSX technology [1]. The CSSX technology utilizes multi-component organic solvent and annular centrifugal contactors to extract Cs-137 from salt waste. In the CSSX process, salt waste is mixed in centrifugal contactors with organic solvent containing Isopar L. The contactors then separate the majority of the cesium-laden solvent from the aqueous solution. Coalescers and decanters process the aqueous Decontaminated Salt Solution (DSS) and Strip Effluent (SE) solutions to allow recovery and reuse of the residual organic solvent remaining in the aqueous solution, and to limit the quantity of solvent available to be transferred to the downstream facilities.

Due to the radiolysis of the aqueous nuclear wastes, hydrogen generation is expected in the MCU holding tanks. In the event of a loss of ventilation, it is possible for the hydrogen to accumulate in the vapor space of a holding tank. With the possible presence of the organic solvent (i.e., Isopar-L), the hydrogen and the vapor of the solvent form a composite flammable gas mixture, resulting in a shorter time to flammability than that of a pure hydrogen environment.

The purpose of this paper is to present the methodology used to evaluate the times-to-Lower Flammability Limit (LFL) and stoichiometric concentration (SC) and the consequences as a result of hydrogen deflagration and, possibly, detonation in the MCU holding tanks. This paper also examines the effect of the organic solvent Isopar-L used in the process on the flammability and consequences.

Description of the Tanks and Input Data

The holding and process tanks considered in this analysis are the Strip Effluent Hold Tank (SEHT), Salt Solution Receipt Tank (SSRT), and Strip Effluent Decanter (SED). These tanks are cylindrical tanks with elliptical heads lying on their longitudinal axis. Some of the key parameters are listed in Table 1. The overflow lines establish the minimum volumes for flammable vapor accumulation. There are additional small cylinders (referred to as "ports") on the tank tops to accommodate the mounting of level control pumps and level instrumentations.

The SED receives aqueous flow with concentrated cesium containing residual solvent that is not completely separated in the centrifugal contactors into the "Large side" of the tank. An underflow weir allows the heavier aqueous solution to pass through to the "Small side" of the tank while retaining the lighter solvent at the liquid surface in the Large side of the tank. Generally, the level in the Large side is at its maximum (i.e. inside the pump port) thus filling the space between the two weirs with liquid. The aqueous solution, minus the solvent then flows over an overflow weir and is pumped out to the SEHT. The SED is depicted in Figure 1; the SSRT and SEHT are similar in design but do not contain underflow and overflow weirs and are not generally maintained at nearly full volume.

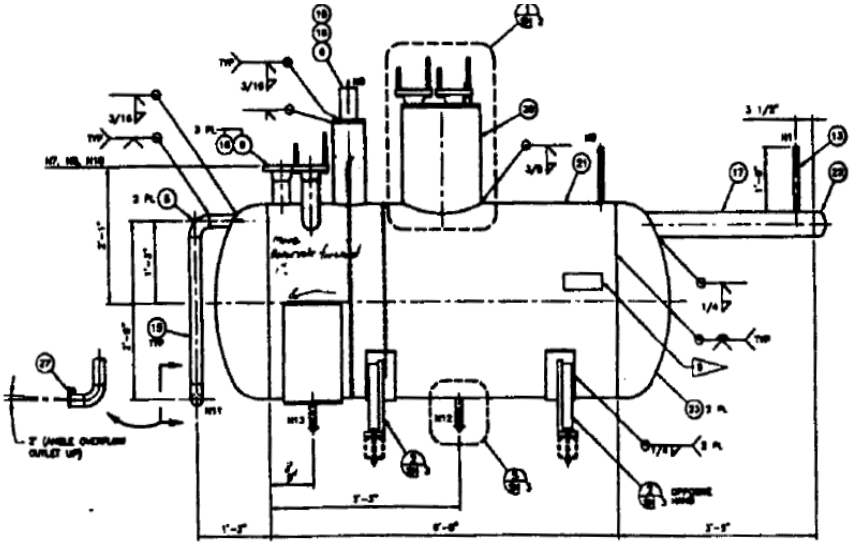

Figure 1 SED Schematic

Table 1 Key Tank Parameters

Parameter	SEHT	SSRT	SED
Cylinder length	9 ft 9 in	19 ft 6 in	6 ft
Diameter	4 ft 4 in	8 ft	3 ft
Number of elliptical heads	2	2	2
Height of head	13 in	25.5 in	12 in
Overflow line position (from top of tank)	6 in	6 in	3 in
Waste stream	Strip Effluent	MCU Feed	Strip Effluent (Upset)
Hydrogen generation rate @ 50°C (ft^3/hr-gal)	1.53×10^{-5}	6.29×10^{-7}	6.80×10^{-5}

The radiological dose resulting from an accident is determined by the radionuclide concentrations (Ci/gal) in the tanks and the Total Effective Dose Equivalent (TEDE) unit dose (rem/Ci). In this analysis, the TEDE unit doses are evaluated by the atmospheric dispersion code MACCS-2 [2] with the Savannah River Site (SRS) specific meteorological data and a 3-minute ground level release duration. The TEDEs are given in Table 2.

Table 2 TEDEs for 3-Minute Ground Release

Waste Stream	Dose (rem/gal)	
	100m Onsite	H-Area Offsite
Strip Effluent (Normal Process)	1.35E-01	1.74E-04
Strip Effluent (Upset Process)	4.65E-01	5.78E-04
MCU Feed	4.58E-02	6.45E-05

Deflagration and Detonation Models

In a tank with its vapor space filled with hydrogen, the energy of combustion is calculated by the product of the number of moles of the hydrogen and its molar combustion energy; i.e.,

$$E_H = N_H \varepsilon_H \quad , \tag{1}$$

where $\in_H$ is the molar combustion energy of hydrogen (= 57.8 x 10^3 cal/mole or 242 kJ/mole) and N_H is the total number of moles of hydrogen, which can be calculated by the Ideal Gas Law:

$$N_H = C_H \frac{P V_V}{\overline{R} T} \ , \tag{2}$$

where

C_H = hydrogen concentration (in volume or mole fraction)
P = Pressure (Pa)
V_V = Vapor volume (m^3)
$\overline{R}$ = Universal Gas Constant (8.3143 J/mole-K)
T = temperature (K).

The time to Lower Flammability Limit (LFL) is calculated by dividing the volume of hydrogen at LFL in the tank by the hydrogen generation rate; i.e.,

$$t_{LFL} = \frac{V_H}{G} = \frac{C_{LFL} V_{V-total}}{G} , \tag{3}$$

where t_{LFL} is the time to LFL, C_{LFL} is the LFL concentration of hydrogen (4%), and G is the hydrogen generation rate, which is given by:

$$G = g' V_{L-total} \tag{4}$$

where g' is the volumetric hydrogen generation rate of the liquid waste (in ft^3/hr-gal). Equation 3 can be also used to determine the time to stoichiometric concentration if the LFL concentration is replaced by the stoichiometric concentration of 29.5%.

If the hydrogen concentration is greater than or equal to the LFL value, this analysis postulates that deflagration will occur. No correction to the LFL is used because a low temperature of 25°C

is assumed to maximize the number of moles of hydrogen. The resultant dose from the deflagration is dependent on the vaporization source term which is given by:

$$ST_d = \frac{F\ E_H}{h_{fg}(1kg/1000g)\,\rho_s\,(3785cc/gal)} \times ARF * RF\ , \qquad \text{(in gal)} \qquad (5)$$

where

E_H = combustion energy (kJ)
h_{fg} = evaporation energy of water (kJ/kg),
ρ_s = density of liquid waste (g/cc), conservatively assumed to be 1.

and F is the fraction of the combustion energy that is deposited into the liquid surface, which is equal to the ratio of the liquid surface area and the total surface areas "seen" by the flame. This analysis conservatively sets F to be 1/2. For the ARF*RF value, DOE Handbook [4] recommends a bounding ARF of 0.1 for venting of superheated liquids with 50-100°C of superheating. The physical mechanisms involved in entrainment by vapor created from surface boiling due to radiant energy deposition (i.e., deflagration) are not exactly the same as those for entrainment of steam created within a volume of liquid, and hence fewer droplets would be created. As a result, it is judged that an ARF value of 0.1 is reasonable and conservative. For deflagration source term calculation, Damage Ratio (DF) and Leak Path Factor (LPF) are set to one.

If the concentration of the hydrogen exceeds the maximum stoichiometric concentration (29.5%), the present analysis uses the TNT model [4] to evaluate the detonation effect. In this model, the mass of liquid (source term) made airborne by the detonation is set equal to the mass of TNT that produces the same energy; i.e.,

$$ST_{TNT} = \frac{E_H(J)}{\varepsilon_{TNT}(J/g)\ \rho_s(g/cc)\ (3785\,cc/gal)}, \qquad \text{(in gal)} \qquad (6)$$

where $\in_{TNT}$ is the specific TNT energy which is 4,606 *J/g* (or 1.1 kcal/g) and ρ_s is the density of the liquid waste. Again, this analysis conservatively uses the water density (1 g/cc) for all detonations. Using the TNT model implies that DR, ARF, RF and LPF are all set to one.

The vapor volume in the source term calculation is the tank volume above the liquid level. For the SED, the Large Side and Small Side are treated separately for the time to LFL/SC calculation and are therefore dependent on the liquid level on either side. The level in the Small Side cannot rise above the overflow line. The level in the Large Side can rise to a maximum level inside the pump port.

For dose calculations, the Large and Small Side vapor spaces are lumped together to be treated as the vapor space for the Large Side (which bounds the dose from the Small Side). The Large Side vapor volume is level dependent. The Small Side is assumed to be empty (including the space between the weirs) thus maximizing the vapor volume and hydrogen content. This is conservative for dose calculations.

Once the source terms are determined, the deflagration and detonation doses can be readily obtained by multiplying the source term (in gal) with the appropriate TEDEs.

Effects of Isopar-L on Flammability

This analysis considers the effects of Isopar-L in the SSRT, SED, and SEHT. Note that Isopar-L is expected to be present in the SED but little is expected to be present in the SSRT or SEHT. Since Isopar-L itself is combustible, its presence could change the composition of the combustible gases in the vapor space of the SEHT, SSRT or SED. The vapor pressure of Isopar-L increases with temperature. This analysis assumes the tanks are initially at 50°C. The vapor pressure of Isopar-L is approximately 4 mm Hg or about 0.53% [5].

For a mixture of Isopar-L and hydrogen, the Composite Lower Flammability Limit (CLFL) can be calculated by using the Le-Chatelier's Law [6]; i.e.,

$$CLFL = \frac{1}{\frac{f_H}{LFL_H} + \frac{f_I}{LFL_I}} \tag{7}$$

where f_H = fraction of hydrogen in fuel
f_I = fraction of Isopar-L in fuel
LFL_H = LFL of hydrogen = 4% [6]
LFL_I = LFL of Isopar-L = 0.6% [7]

With the Isopar-L concentration at 0.53%, it can be shown that the fuel concentration exceeds the CLFL when the hydrogen concentration is 0.48% [9].

Since time-to-deflagration is directly proportional to the hydrogen concentration, the ratio of time-to-deflagration of the Isopar-L/hydrogen mixture to that of pure hydrogen is:

$$\frac{t_f}{t_{LFL}} = \frac{0.48}{4} = 0.12 \tag{8}$$

This means that the presence of Isopar-L leads to a reduction of 88% in time to deflagration. The ratio of combustion energy resulting from the deflagration of the Isopar-L/hydrogen mixture to that of pure hydrogen is:

$$\frac{E_{mix}}{E_H} = \frac{n'_H \varepsilon_H + n'_I \varepsilon_I}{n_H \varepsilon_H}, \tag{9}$$

where n_H = hydrogen concentration at LFL = 4 volume%
n'_H and n'_I = hydrogen and Isopar-L concentrations at CLFL, respectively.
ε_H = hydrogen heat of combustion = 242 kJ/mole [6]
ε_I = Isopar-L heat of combustion = 8,061 kJ/mole [8]

Since the gas concentration is directly proportional to the number of moles, it can be shown that the combustion energy, and the subsequent consequences, resulting from the deflagration of the Isopar-L/hydrogen mixture at CLFL is 4.5 times of that of the pure hydrogen at LFL [9].

It has been determined that the volume percent of Isopar-L in a stoichiometric mixture with air is 1.22% [8]. The oxygen left after an stoichiometric combustion is zero. At 50°C, the Isopar-L concentration is 0.53% volume. The amount of oxygen consumed is approximately 9.1% (i.e., $21 \times 0.53 / 1.22$) and the amount of oxygen left is 11.9%. In a stoichiometric pure hydrogen-air mixture, the hydrogen concentration is 29.5% volume. For a mixture with 11.9% oxygen, the

stoichiometric hydrogen concentration is approximately 16.7% (i.e. 29.5 x 11.9 / 21). Therefore, the time to fill this space with hydrogen is

$$\frac{t\ (Isopar + H_2)}{t\,(H_2)} = \frac{16.7}{29.5} = 0.57 \qquad (10)$$

or 57% of the time to fill it with 29.5% hydrogen. In terms of energy generated by detonation, the ratio of energy from an Isopar/hydrogen/air mixture at 50°C to that from a stoichiometric hydrogen/air mixture can be evaluated in a fashion similar to Equation 9. However, it is conservative to assume the Isopar-L is at its stoichiometric concentration (i.e. 1.22%). The energy ratio is therefore

$$\frac{Energy\ (Isopar)}{Energy\ \ (H_2)} = \frac{n_I^*\ \varepsilon_I}{n_H^*\ \varepsilon_H} = \frac{1.22\ (8061)}{29.5\ (242)} = 1.38 \qquad (11)$$

where n_I^* = Isopar-L stoichiometric concentration = 1.22 volume%
n_H^* = hydrogen stoichiometric concentration = 29.5 volume%

which is used to "correct" the energy generated by the detonation of a pure hydrogen-air mixture.

Results of Analysis

A summary of the calculation for pure hydrogen-air mixtures is given in the following Tables 3 to 5. The maximum liquid levels are established by the overflow lines except for the SED Large Side which is the normal operating level inside the pump port. The effects of Isopar-L is summarized in Tables 6 to 8.

Table 3 Calculation Results for Hydrogen-Air Mixture in SEHT

Level	Time to LFL	Dose (rem)		Time to SC	Dose (rem)	
(inches)	(hours)	Onsite	Offsite	(hours)	Onsite	Offsite
2	2.98E+04	1.45E-03	1.86E-06	2.20E+05	1.05E-01	1.35E-04
6	5.41E+03	1.38E-03	1.77E-06	3.99E+04	9.94E-02	1.28E-04
12	1.71E+03	1.22E-03	1.56E-06	1.26E+04	8.79E-02	1.13E-04
18	8.03E+02	1.02E-03	1.31E-06	5.92E+03	7.37E-02	9.49E-05
24	4.27E+02	8.05E-04	1.04E-06	3.15E+03	5.82E-02	7.49E-05
30	2.33E+02	5.86E-04	7.54E-07	1.72E+03	4.23E-02	5.45E-05
36	1.21E+02	3.76E-04	4.83E-07	8.90E+02	2.72E-02	3.49E-05
40	7.13E+01	2.48E-04	3.19E-07	5.26E+02	1.79E-02	2.31E-05
44	3.59E+01	1.36E-04	1.75E-07	2.65E+02	9.85E-03	1.27E-05

Overflow is at 43 inches.

Table 4 Calculation Results for Hydrogen-Air Mixture in SSRT

Level	Time to LFL	Dose (rem)		Time to SC	Dose (rem)	
	(hours)	Onsite	Offsite	(hours)	Onsite	Offsite
2	1.84E+06	3.35E-03	4.73E-06	1.36E+07	2.42E-01	3.42E-04
10	1.55E+05	3.19E-03	4.50E-06	1.14E+06	2.31E-01	3.25E-04
20	4.97E+04	2.88E-03	4.05E-06	3.67E+05	2.08E-01	2.93E-04
40	1.32E+04	2.05E-03	2.89E-06	9.73E+04	1.48E-01	2.09E-04
60	4.36E+03	1.14E-03	1.61E-06	3.22E+04	8.26E-02	1.16E-04
80	9.97E+02	3.53E-04	4.98E-07	7.35E+03	2.56E-02	3.60E-05
88	3.28E+02	1.25E-04	1.76E-07	2.42E+03	9.03E-03	1.27E-05

Overflow is at 87 inches.

Table 5 Calculation Results for Hydrogen-Air Mixture in SED

Level	Time to LFL (hrs)		Dose (rem)		Time to SC (hrs)		Dose (rem)	
(inches)	Large side	Small side	Onsite	Offsite	Large side	Small side	Onsite	Offsite
2	4.07E+03	2.51E+02	1.66E-03	2.06E-06	2.30E+04	1.85E+03	1.20E-01	1.49E-04
6	7.15E+02	1.69E+02	1.57E-03	1.95E-06	5.27E+03	1.25E+03	1.14E-01	1.41E-04
10	2.96E+02	1.22E+02	1.46E-03	1.81E-06	2.18E+03	8.28E+02	1.05E-01	1.31E-04
14	1.54E+02	7.37E+01	1.32E-03	1.64E-06	1.14E+03	5.43E+02	9.53E-02	1.18E-04
18	8.71E+01	4.70E+01	1.17E-03	1.46E-06	6.43E+02	3.47E+02	8.49E-02	1.05E-04
22	5.01E+01	2.85E+01	1.03E-03	1.28E-06	3.70E+02	2.10E+02	7.44E-02	9.25E-05
26	2.78E+01	1.57E+01	8.94E-04	1.11E-06	2.05E+02	1.15E+02	6.46E-02	8.02E-05
32	9.25E+00	3.94E+00	7.28E-04	9.05E-07	6.82E+01	2.91E+01	5.27E-02	6.54E-05
36	4.24E+00	NA	6.71E-04	8.34E-07	3.13E+01	NA	4.85E-02	6.03E-05
48	1.70E+00	NA	6.39E-04	7.94E-07	1.25E+01	NA	4.62E-02	5.74E-05

Maximum level is 40 inches for the Large side and 33 inches for the Small side

Table 6 Effect of Isopar-L on SEHT

	H_2 Only		H_2 and Isopar-L	
	100m Onsite	H-Area Offsite	100m Onsite	H-Area Offsite
Time to Deflagration (for max dose) (hr)	2.98E+04		3.58E+03	
Maximum Deflagration Dose (rem)	1.45E-03	1.86E-06	6.53E-03	8.37E-06
Minimum Time to Deflagration (level at overflow line) (hr)	44.0		5.28	
Deflagration Dose (at min time) (rem)	1.63E-04	2.10E-07	7.34E-04	9.43E-07
Time to Detonation (for max dose) (hr)	2.20E+05		1.25E+05	
Maximum Detonation Dose (rem)	1.05E-01	1.35E-04	1.44E-01**	1.85E-04**
Minimum Time to Detonation (level at overflow line) (hr)	324		185	
Detonation Dose (at min time) (rem)	1.18E-02	1.52E-05	1.61E-02**	2.08E-05**

** Stoichiometric Isopar-L only.

Table 7 Effect of Isopar-L on SSRT

	H_2 Only		H_2 and Isopar-L	
	100m Onsite	H-Area Offsite	100m Onsite	H-Area Offsite
Time to Deflagration (for max dose) (hr)	1.843E+06		2.21E+05	
Maximum Deflagration Dose (rem)	3.35E-03	4.73E-06	1.51E-02	2.13E-05
Minimum Time to Deflagration (level at overflow line) (hr)	3.97E+02		4.76E+01	
Deflagration Dose (at min time) (rem)	1.50E-04	2.12E-07	6.75E-04	9.54E-07
Time to Detonation (max) (hr)	1.360E+07		7.75E+06	
Maximum Detonation Dose (rem)	2.42E-01	3.42E-04	3.32E-01**	4.69E-04**
Minimum Time to Detonation (level at overflow line) (hr)	2.93E+03		1.67E+03	
Detonation Dose (at min time) (rem)	1.09E-02	1.53E-05	1.49E-02**	2.09E-05**

** Stoichiometric Isopar-L only.

Table 8 Effect of Isopar-L on SED

	H_2 Only		H_2 and Isopar-L	
	100m Onsite	H-Area Offsite	100m Onsite	H-Area Offsite
Time to Deflagration (max dose) (hr)	2.51E+02		3.01E+01	
Maximum Deflagration Dose (rem)	1.66E-03	2.06E-06	7.47E-03	9.27E-06
Minimum Time to Deflagration (max level in pump port) (hr)	1.70		0.20	
Deflagration Dose (at min time) (rem)	6.39E-04	7.94E-07	2.86E-03	3.57E-06
Time to Detonation (max dose) (hr)	1.85E+03		1.06E+03	
Maximum Detonation Dose (rem)	1.20E-01	1.49E-04	1.64E-01**	2.04E-04**
Minimum Time to Detonation (max level in pump port) (hr)	12.5		7.13	
Detonation Dose (at min time) (rem)	4.62E-02	5.74E-05	6.33E-02**	7.86E-05**

** Stoichiometric Isopar-L only.

Conclusion

Based on the results of this analysis, it can be seen that SED and SSRT respectively have the shortest and longest times to flammability. Depending on the temperature, the presence of the Isopar-L can significantly further decrease the time to deflagration or detonation. For radiological consequences, neither the deflagration nor detonation event results in doses that

exceed or challenge the Evaluation Guideline (100 rem onsite, 25 rem offsite) for any one of the tanks at any liquid level.

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